Electron cyclotron resonance plasma etching of Si with Cl\textsubscript{2}: plasma chemistry and mechanisms

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Abstract. Electron cyclotron resonance (ECR) plasma etching of Si with Cl\textsubscript{2} has been investigated from the viewpoint of plasma chemistry. Experiments were performed over a wide pressure range (0.2-10 mTorr), using a divergent magnetic-field ECR plasma reactor supplied with 2.45-GHz microwave input powers; a floating electrode or substrate holder was located ~30 cm downstream (B=150 G) from the 875-G ECR resonance region, and samples of polycrystalline Si were etched with no additional wafer biasing. Several diagnostics were employed to characterize the plasma around the wafer position: two-photon laser-induced fluorescence (LIF), optical emission spectroscopy, microwave interferometry, and electrical measurements with Langmuir probes and a retarding grid analyzer. Moreover, chemical kinetics in Cl\textsubscript{2} plasmas were modeled to gain an insight into the LIF and optical emission measurements, and to know chemical compositions in ECR Cl\textsubscript{2} plasmas. Attention was then focused on neutral Cl atom fluxes and ion energies and fluxes onto the substrate, and on their correlations with the etching characteristics such as etch rates and profiles. The etch rate behavior is interpreted in terms of a modified adsorption-reaction-ion stimulated desorption process, and some lateral etching after an overetch step in terms of the incoming ion trajectories.

1. Introduction

As the integrated circuit device dimensions continue to drop below 0.5 μm and the gate oxide thicknesses drop to 100 Å or less, great demands are still being made on plasma etching technology giving higher directionality, higher selectivity, and less damage. Electron cyclotron resonance (ECR) is one of several plasma-generation techniques that have been developed to meet these demands. Most of such sources are designed to operate at lower gas pressures with magnetic fields, resulting in higher-density, higher-temperature plasmas independent of wafer biasing. To understand and control critical parameters responsible for processing in ECR plasmas, extensive work has focused on the behavior of charged particles such as ions and electrons [1-5]. In contrast, little or no attention has been paid to reactive neutrals, which are generally assumed to play an important role in many etching processes; in effect, it may be difficult to quantitatively measure the concentrations of reactive neutral species under typical ECR processing conditions.

This paper presents plasma chemical aspects of the ECR chlorine plasma etching of Si; in practice, Si etching with Cl\textsubscript{2} is not only a relatively simple process, but also an important one to achieve highly directional, highly selective etching of Si over SiO\textsubscript{2} without surface inhibitors. In our studies, the concentrations of atomic Cl, the principal neutral reactant in Cl\textsubscript{2} plasmas, were measured by two-photon laser-induced fluorescence (LIF) [6]. Modeling calculations of chemical kinetics in ECR Cl\textsubscript{2} plasmas were also made taking account of a number of electron-impact events and ion reactions. The numerical results gave a quantitative understanding of chemical compositions in ECR plasmas, being compared with the measured Cl concentrations. These results, together with electrical measurements of ion and electron energies and densities, yielded neutral Cl fluxes and ion energies and fluxes onto the substrate, which are reduced parameters that primarily govern the etching characteristics. Moreover, a modified adsorption-reaction-ion stimulated desorption process is discussed to interpret the Si etch rate behavior,
and some lateral etching observed after an overetch step is interpreted in terms of the incoming ion trajectories affected by localized charging of pattern features. This is a preliminary effort to qualify the role of reactive neutrals as well as that of ions in low-pressure, high-density plasma processing.

2. Experiment

Figure 1 shows the experimental setup which has been detailed elsewhere [5,6]. Briefly, the ECR plasma reactor consisted of two grounded stainless-steel chambers: a water-cooled plasma chamber 20 cm in diameter and 50 cm long, and a specimen chamber 35 cm in diameter and 45 cm long. Four solenoid coils were set around the former, providing a divergent magnetic field to produce ECR plasmas and transport them to a sample for etching in the specimen chamber. The discharge was established by 2.45-GHz right-hand circularly polarized microwaves of TE$_{11}$ mode, fed to the plasma chamber via a 10-cm-diam quartz window; the 875-G ECR resonance was located at an axial position $z$=42 cm from the microwave entrance, near the end of the plasma chamber. Pure Cl$_2$ gas was introduced into the reactor, evacuated down to a base pressure $<10^{-6}$ Torr, through a set of small holes around the entrance window. The specimen chamber had an end port for pumping and side ports for diagnostics, containing a 17-cm-diam floating electrode or substrate holder at $z$=75 cm, -33 cm downstream ($B=150$ G) from the ECR resonance region. Experiments were performed at an incident microwave power of 900 W (0.068 W/cm$^2$) and a Cl$_2$ gas flow rate of 10 standard cm$^3$/min; the reactor gas pressure was varied from $P_r=10$ to 0.2 mTorr (1.33 to 0.0266 Pa), and the corresponding gas residence time in the specimen chamber was estimated to be of the order of $\tau_0=3.4-0.068$ s.

Several diagnostics were employed to characterize the plasma around the wafer position: two-photon LIF, optical emission spectroscopy, microwave interferometry, and electrical measurements with Langmuir probes and a retarding grid analyzer. The LIF measurements sampled a portion of the discharge on axis ~2.5 cm upstream from the electrode. In our LIF measurements [6], ground-state Cl atoms were excited by two-photon absorption of 233.2-nm laser radiation, and the fluorescence of Cl was observed at 725.6 nm. Absolute calibration was achieved to obtain the Cl concentrations, by generating Cl atoms through UV photolysis of CCl$_4$ molecules with the same laser radiation. A microwave interferometer operated at 24 GHz was used to monitor the line-averaged plasma electron density, and optical emissions were also monitored routinely in these experiments. Moreover, planar Langmuir probes were employed to measure the ion density, electron temperature, and the plasma and floating potentials. A retarding grid analyzer was set in place of the substrate holder, measuring the flux and energy distribution of positive ions directed toward the substrate on axis [5].

Samples for etching were 6-in.-diam single-crystal Si wafers with a 1000-Å-thick layer of thermally grown SiO$_2$ and then a 3000-Å-thick layer of heavily P-doped polycrystalline Si, masked with a 1-µm-thick photoresist pattern of lines and spaces. The samples were clamped into place on the electrode whose temperature was controlled by circulating coolant fluid, and backside helium was injected for increased wafer thermal contact. The etched depth was measured by a stylus gauge, and the vertical etch rate was calculated as the ratio of the etched depth to the total etching time. Moreover, the etched profile was examined with a scanning electron microscope (SEM). In these experiments, prior to main etching under floating substrate conditions, an additional rf biasing at 13.56 MHz was used during a brief pre-etch breakthrough step to remove a native oxide layer.

![Fig. 1 Experimental setup.](image_url)
3. Results of Plasma Characterization

Figure 2 shows the electrical measurements of ion and electron energies and densities on axis around the wafer position as a function of Cl₂ pressure $P_0$: (a) the plasma electron density $n_e$ and temperature $T_e$; (b) the plasma potential $V_p$ and the difference $V_p-V_f$ between the plasma and floating potentials; and (c) the ion flux $\Gamma_i$ and the peak ion energy $E_i$ toward the substrate. Here, the ion energies $E_i$ measured by a retarding grid analyzer are in agreement with the potential differences $V_p-V_f$ measured by a Langmuir probe, which correspond to the sheath potentials $V_s$ at the floating substrate. Moreover, the measured ion fluxes $\Gamma_i$ are consistent with the $\Gamma_i$ values calculated using the Bohm criterion [7] with the measured $n_i$ ($=n_e$) and $T_e$: $\Gamma_i = 0.6n_i(kT_e/m_i)^{1/2}$, where $n_i$ is the ion density, $k$ is Boltzmann’s constant, and $m_i$ is the ion mass (assuming Cl₂⁺ ions are predominant). As $P_0$ is decreased, the plasma density increases from $n_e = 10^{10}$ to $10^{11} \text{ cm}^{-3}$, peaks at $P_0=0.4 \text{ mTorr}$, and then decreases; the electron temperature increases continuously from $T_e=2.5$ to 9 eV. Correspondingly, the plasma potential $V_p$ and the potential difference $V_p-V_f$ increase significantly with decreasing $P_0$. The ion energy ranges from $E_i=10$ to 70 eV, and the ion flux toward the substrate ranges from $\Gamma_i = 0.16$ to 2.5 mA/cm², corresponding to $= 0.10$ to $1.6\times10^{16}$ ions/cm².

The optical emission intensities of several atomic lines and molecular bands of Cl, Cl⁺, Cl₂, and Cl₂⁺, measured around the wafer position, are also shown in Fig. 2(d). It is noted here that the emission intensity of Cl₂ decreases with decreasing $P_0$, while that of Cl⁺ increases significantly; on the other hand, the Cl and Cl₂⁺ intensities exhibit relatively little changes over the $P_0$ range studied. The decreased Cl₂ intensity at lowered $P_0$ may be related to a decrease in the feedstock Cl₂ gas density, and the increased Cl⁺ intensity to an increase in $T_e$.

![Fig. 2](image-url)
Fig. 3 (a) Cl atom concentration [Cl] and (b) ratio \( \Gamma_{\text{Cl}}/T_i \) of neutral Cl flux to ion flux toward the substrate as a function of Cl\(_2\) pressure \( P_0 \). In (a), the solid squares are the two-photon LIF measured data on axis around the wafer position, while the open circles represent the results of modeling calculations of chlorine chemical kinetics.

Figure 3(a) shows the Cl atom concentration [Cl] as a function of Cl\(_2\) pressure \( P_0 \). Here, the solid squares represent the measured data on axis around the wafer position by two-photon LIF; the measurement and absolute calibration techniques have been detailed in [6]. Unfortunately, our LIF measurements could not be made at lower pressures, \( P_0 < 0.5 \) mTorr, owing to deteriorated signal-to-noise problems due to increased fluctuation of increased background plasma emission. The Cl concentration measured ranges from \([\text{Cl}] = 2 \times 10^{12}\) to \(3 \times 10^{13}\) cm\(^{-3}\), decreasing with decreasing \( P_0 \). The corresponding Cl fractions, \([\text{Cl}]/[\text{Cl}_2]\), are estimated to be between \( =1 \) and \(2 \)% (assuming the gas temperature \( T = 300\) K). From the concentration of Cl atoms and their thermal velocity, the flux \( \Gamma_{\text{Cl}} \) of Cl atoms directed to the substrate can be calculated as \( \Gamma_{\text{Cl}} = (1/4)[\text{Cl}](8kT/\pi m)^{1/2} \), assuming [Cl] to be uniform in space. 

The neutral Cl flux thus calculated ranges from \( \Gamma_{\text{Cl}} = 3 \times 10^{16}\) atoms/cm\(^2\)s.

The ratio of ion flux to neutral flux striking the substrate, or its inverse, is one of reduced parameters that primarily govern the etch rate and anisotropy. From the above Cl concentration measurements and the electrical measurements of ion and electron energies and densities in Fig. 2, the ratio of neutral Cl flux to ion flux toward the substrate, \( \Gamma_{\text{Cl}}/T_i \), can be evaluated as shown in Fig. 3(b). Our measurements demonstrate that the neutral-to-ion flux ratio in ECR decreases almost linearly with decreasing pressure, from \( \Gamma_{\text{Cl}}/T_i = 30 \) at \( P_0 = 10\) mTorr to 0.3 at \( P_0 = 0.5\) mTorr.

4. Chemical Kinetics Model

A preliminary model of chemical kinetics in ECR Cl\(_2\) plasmas was assembled from reactions which have been known in the literature, together with others assumed to occur by comparison with reactions of homologous molecules. The species included in the model are Cl\(_2\), Cl, Cl\(^+\), Cl\(^-\), Cl\(^{++}\), and Cl\(^-\), and a summary of their electron-impact events and ion reactions are listed in Table 1, together with the excitation thresholds \( E_{\text{in}} \). In ECR plasmas, electron-ion recombination processes, except dissociative one, may be unimportant owing to high electron temperatures \( T_e \); the electron attachment, leading to Cl\(^-\) negative ions, is also unlikely to occur in binary electron-molecule collisions at low pressures \( P_0 \).

Cross sections for the reaction processes concerned here are not well known. As for electron-impact events, only the following shown in Fig. 4 have been directly measured as a function of electron energy \( E_e \): \( \sigma_e = (\sigma_i + \sigma_j + \sigma_k) \), the total ionization cross section for Cl\(_2\) [8]; \( \sigma_{e0} = (\sigma_j + \sigma_k) \), the total cross section for negative-ion formation from Cl\(_2\) [8]; \( \sigma_{e0} \), the cross section for ionization of Cl [9]; and \( \sigma_{i} \), the cross section for ionization of Cl\(^-\) [10]. The respective cross sections \( \sigma_{i} \) \((i=1-4)\) for ionization and attachment may be determined as follows, from the \( \sigma_e \) and \( \sigma_{e0} \) on referring to relative photoionization yields of Cl\(_2^+\), Cl\(^+\), and Cl\(^-\) from Cl\(_2\) in the vacuum UV [10,11]: 

\[
\begin{align*}
\sigma_1 &= \sigma_e - (\sigma_2 + \sigma_3), \\
\sigma_2 &= \sigma_e (E_e - 4.0)/4, \\
\sigma_3 &= \sigma_e \\
\end{align*}
\]
Electron cyclotron resonance plasma etching of Si with Cl₂

<table>
<thead>
<tr>
<th>Reaction process</th>
<th>$E_{th}$ (eV)</th>
<th>$\sigma$ (cm²)</th>
<th>$k$ (cm³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular ionization</td>
<td>e+Cl₂ → Cl₂⁺+e+e</td>
<td>11.48</td>
<td>$\sigma_1$</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>e+Cl₂ → Cl⁺+Cl⁺+e+e</td>
<td>15.48</td>
<td>$\sigma_2$</td>
</tr>
<tr>
<td>Ion-pair formation</td>
<td>e+Cl₂ → Cl⁺+Cl⁺+e</td>
<td>11.87</td>
<td>$\sigma_3$</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>e+Cl₂ → (Cl₂⁻)⁺⁺Cl⁻+Cl⁻</td>
<td>0</td>
<td>$\sigma_4$</td>
</tr>
<tr>
<td>Dissociative excitation</td>
<td>e+Cl₂ → Cl⁺+Cl⁺+Cl⁻+e</td>
<td>3.12</td>
<td>$\sigma_5$</td>
</tr>
<tr>
<td>Atomic ionization</td>
<td>e+Cl⁺ → Cl⁺⁺+e+e</td>
<td>13.01</td>
<td>$\sigma_6$</td>
</tr>
<tr>
<td></td>
<td>e+Cl⁺ → Cl⁺⁺+e+e</td>
<td>23.80</td>
<td>$\sigma_7$</td>
</tr>
</tbody>
</table>

| Ion-ion recombination                   | Cl⁺⁺+Cl⁺⁺ → Cl⁺⁺Cl⁺⁺ | $k_{5}=5\times10^{-8}$ cm³/s |
| Dissociative recombination              | Cl⁺⁺+Cl⁺⁺ → Cl⁺⁺Cl⁺⁺ | $k_{10}=9\times10^{-7}/T_{e}^{0.6}$ cm³/s |
| Volume recombination                    | Cl⁺⁺+Cl⁺⁺ → (1/2)Cl⁺⁺+Cl⁺⁺ | $k_{7}=2.8\times10^{-12}$ cm³/s |
| Wall recombination                      | Cl⁺⁺+Cl⁺⁺ → (1/2)Cl⁺⁺+Cl⁺⁺ | $k_{7}=2.8\times10^{-12}$ cm³/s |

for $E_{th}>11.87$ eV, and $\sigma_{x}=Q_{x}$ for $E_{th}<11.87$ eV. Moreover, the cross section $\sigma_{x}$ for dissociative excitation of Cl₂ has been given by Rogoff et al. [13] through Boltzmann-equation calculations of electron swarm parameters for Cl₂; special attention will be given to this $\sigma_{x}$ later. From these cross sections $\sigma_{x}$ ($x=1-7$), the corresponding rate coefficients $k_{x}$ were evaluated as a function of $T_{e}$ as shown in Fig. 5, assuming a Maxwellian electron energy distribution. It is noted here that the dissociative attachment, generating Cl⁻ negative ions and neutral Cl atoms, is significant ($k_{4}>k_{1}, k_{5}$) at low $T_{e}$.

Cross sections or rate coefficients for the ion reactions are less well known. The ion-ion recombination rate for Cl⁺⁺+Cl⁺⁺ has been measured to be $k_{5}=5\times10^{-8}$ cm³/s at $T_{e}=300$ K [14]; the Cl⁺⁺+Cl⁺⁺ recombination rate $k_{10}$ may also be large and comparable to $k_{4}$ for Cl⁺⁺+Cl⁻ [13]. The dissociative recombination rate for Cl⁺⁺ was taken to

Fig. 4 Cross sections for electron-impact processes in chlorine that have been known in the literature: $Q_{x}$, the total ionization cross section for Cl₂; $Q_{n}$, the total cross section for negative ion formation from Cl₂; $\sigma_{x}$, the cross section for dissociative excitation of Cl₂; $\sigma_{x}$, the ionization cross section for Cl₂; and $\sigma_{x}$, the ionization cross section for Cl⁺⁺.

Fig. 5 Rate coefficients $k_{x}$ ($x=1-7$) for electron-impact processes in chlorine as a function of electron temperature $T_{e}$, evaluated assuming a Maxwellian electron energy distribution.
be similar to that for Ar\textsuperscript{+} at T=300 K \cite{15}: \( k_{o}=9\times10^{-7}/T_{e}^{0.6} \) cm\textsuperscript{3}/s with \( T_{e} \) in eV. In addition, as for ion reactions of chlorine, the cross section for Cl\textsubscript{2}+Cl\textsubscript{2} symmetric charge exchange has been given at high ion energies \( E_{i}>100 \) eV \cite{16}, however, that for Cl\textsuperscript{+}+Cl\textsubscript{2} asymmetric one, probably significant at low \( E_{i} \), is not available. The cross section for Cl\textsuperscript{+}+Cl\textsubscript{2} asymmetric charge exchange has also been measured as a function of \( E_{i} \), together with the electron detachment cross section for Cl\textsuperscript{+}+Cl\textsubscript{2} \cite{17}. Such charge exchange processes were not taken into account in the present model, owing to their less effects on the chemical compositions.

As for loss mechanisms for neutral Cl atoms, the rate coefficient for gas-phase recombination has been measured to be \( k_{r}=2.8\times10^{-32} \) cm\textsuperscript{6}/s at \( T=300 \) K \cite{18}. Under low-pressure ECR plasma conditions, however, the neutral gas-phase chemistry is unimportant in view of small termolecular collision rates. As a result, diffusion to the chamber walls, where recombination and/or adsorption takes place, is the dominant loss process for Cl in ECR.

Given the measured \( n_{e} \) and \( T_{e} \) in Fig. 2(a) and the feedstock gas density \([\text{Cl}_{2}]_{o}\), a set of 5 steady-state rate equations for Cl, Cl\textsuperscript{+}, Cl\textsuperscript{2+}, Cl\textsuperscript{3+}, and Cl\textsuperscript{-} were solved numerically, together with 2 equations for charge neutrality and species conservation. The diffusion problem from the gas phase to the chamber walls was treated as a characteristic decay time: \( \tau_{d} \), for neutral Cl was given by an approximation of Chantry \cite{19} with the known diffusion coefficient \( D_{0} \) of Cl in Cl\textsubscript{2} \cite{20}; \( \tau_{d}=(A_{d}^{2}/D)+(V/A)2(2-\alpha)/\nu\alpha \), where \( A_{d} \) is the diffusion length determined by the container geometry, \( V/A \) the volume-to-surface-area ratio of the container, \( \nu \) the thermal velocity of Cl, and \( \alpha \) the sticking probability of Cl at the walls (0≤\( \alpha \)≤1). Assuming the specimen chamber to be a cylindrical container, the neutral decay time was evaluated to range from \( \tau_{d}=1.4 \) ms at \( P_{0}=10 \) mTorr to 0.083 ms at \( P_{0}=0.2 \) mTorr. It is noted that \( \tau_{d}<<\tau_{r} \), the gas residence time. The decay times \( \tau_{d} \) for ions were taken to be the same for all ionic species. In the calculations thus achieved, the respective species concentrations \([\text{Cl}_{2}]\), \([\text{Cl}]\), \([\text{Cl}_{2}^{+}]\), \([\text{Cl}^{+}]\), \([\text{Cl}^{2+}]\), and \([\text{Cl}^{-}]\) were obtained with the ionic decay time \( \tau_{i} \).

The calculated and measured Cl concentrations are compared in Fig. 3(a). Here, the calculations were made assuming the sticking probability \( \alpha=1 \) at the walls, that is, all Cl atoms onto the surfaces are recombined and/or adsorbed. Agreement between the calculated and measured values was not obtained when using the original rate coefficient \( k_{r} \) or cross section \( \sigma_{r} \) for dissociative excitation of Cl\textsubscript{2}; in effect, the agreement was obtained by lowering \( \sigma_{r} \) by about an order of magnitude. In the present comparison, the agreement is not sufficient at lower \( P_{0}<1 \) mTorr. However, it may be concluded that the presently known cross section \( \sigma_{r} \) for dissociative excitation of Cl\textsubscript{2} is excessively large, by about an order of magnitude.

Figure 6 shows the chemical compositions in ECR Cl\textsubscript{2} plasmas, obtained numerically with \( \sigma_{r}=0.1 \) as a function of pressure \( P_{0} \). The ionic decay times calculated were between \( \tau_{i}=15 \) and 4.6 \( \mu \)s, decreasing with decreasing \( P_{0} \). It may be noted that in our ECR plasmas, molecular Cl\textsuperscript{+} ions are still more abundant than atomic Cl\textsuperscript{+} ions; moreover, Cl\textsuperscript{-} negative ions are less abundant than plasma electrons, which is in contrast to the situation generally appreciated for rf discharges at high pressures \cite{21}.

Fig. 6 Species concentrations \([\text{Cl}_{2}]\), \([\text{Cl}]\), \([\text{Cl}_{2}^{+}]\), \([\text{Cl}^{+}]\), \([\text{Cl}^{2+}]\), and \([\text{Cl}^{-}]\), obtained numerically with \( \alpha=1 \) and \( \sigma_{r}=0.1 \) for different Cl\textsubscript{2} pressures \( P_{0} \). Also shown are the measured \( n_{e} \) and the feedstock gas density \([\text{Cl}_{2}]_{o}\).
5. Etch Rates and Profiles

Figure 7 shows the etch rate of polycrystalline Si as a function of Cl₂ pressure $P_0$, where the solid squares represent the measured data. In these experiments, poly-Si etch rates of 1000–2000 Å/min were obtained in combination with poly-Si/SiO₂ selectivities of >50. As $P_0$ is decreased, the etch rate increases, peaks at $P_0=0.5$ mTorr, and then decreases. This $P_0$ dependence is similar to that of the ion flux $\Gamma_i$ onto the substrate in Fig. 2(c).

In general, a simple ion-assisted reaction model [22] that accounts for the etch rate behavior assumes that the etch yield per ion is proportional to the ion energy $E_i$ and the surface coverage $\Theta$ of reactive neutral species: $R = a\Theta E_i \Gamma_i$. Moreover, the reaction probability of neutrals is assumed to be proportional to the number of bare sites on the surface: $R = bS_b(1-\Theta)\Gamma_C$, where $S_b$ is the sticking probability on a bare surface. Thus, the etch rate $R$ may be expressed as a function of ion energy and ion and neutral Cl fluxes as follows: $R = \frac{aE_i^{0.5} \Gamma_i}{(1+aE_i^{0.5} \Gamma_i/(bS_b \Gamma_C))}$, where the energy dependence is taken to be $E_i^{0.5}$ [1] because of low ion energies in ECR plasmas. Here, the two constants $a$ and $bS_b$ may be determined from the measured data on $R$, $E_i$, $\Gamma_i$, and $\Gamma_C$ under two different conditions, e.g., at $P_0=3$ and 5 mTorr. However, this expression could not fit the measured etch rates at lower pressures, $P_0 \leq 1$ mTorr, as shown in Fig. 7 with $\eta=0$. Under ECR plasma conditions where the ion-to-neutral flux ratio is large ($\Gamma_i/\Gamma_C > 1$) and the ion energy is low ($E_i < 20$ eV), we may assume that the incoming low-energy ions as well as neutrals are adsorbed on surfaces with the same $S_b$ to form reaction products; then, $R = \frac{aE_i^{0.5} \Gamma_i}{(1+aE_i^{0.5} \Gamma_i/(bS_b \Gamma_C(1+\eta \Gamma_i/\Gamma_C)))}$, where $\eta=0$ corresponds to adsorbate formation by neutrals only, and $\eta=1$ to by ions and neutrals. The expression thus assumed fits the measured etch rates over a relatively wide $P_0$ range, as shown in Fig. 7 with $\eta=1$; the disagreement at much lower $P_0 < 0.5$ mTorr could not be explained at the present stage.

The etched profiles obtained were nearly anisotropic with the photoresist largely intact over the $P_0$ range studied, as shown in Fig. 8, exhibiting no undercutting or signature of purely chemical etching; this is in contrast to the conventional and magnetron-enhanced reactive ion etching [23]. Such highly directional, highly selective etching in ECR is ascribed primarily to high ion-to-neutral flux ratios onto the substrate and to low energies of the incoming ions. In practice, however, some lateral etching like bowing and notching was observed after an overetch step particularly at higher $P_0$, as can be seen in (b) of this figure. The mechanism for such lateral etching in ECR may be the result of localized charging of pattern features [22,24,25]: differential charging occurs for insulating microstructures as a result of the differential angular distributions of incoming ions and electrons, and the electron charge establishes an electrostatic potential profile on the sidewalls that is large enough to affect the ion trajectories; thus, the incoming ions tend to be deflected laterally toward the sidewalls, striking near the bottom.

![Fig. 7 Etch rate of polycrystalline Si as a function of Cl₂ pressure $P_0$. The solid squares are the measured data, while the open circles and squares represent the results from etch rate models taking account of an adsorption-reaction-ion stimulated desorption process.](image)

![Fig. 8 SEM micrographs of the etched profile of polycrystalline Si after a 200 % overetch step, obtained at (a) $P_0=0.5$ mTorr and (b) $P_0=1$ mTorr.](image)
6. Conclusions

Atomic chlorine concentrations in ECR Cl₂ plasmas have been measured by two-photon LIF technique. The Cl concentration ranged from $[\text{Cl}] = 2 \times 10^{12}$ to $3 \times 10^{11}$ cm$^{-3}$, decreasing with decreasing pressure $P_o$; the corresponding Cl fractions, $[\text{Cl}] / [\text{Cl}_2]$, were estimated to be between 1 and 2 %. These results, together with electrical measurements of ion and electron energies and densities, demonstrated that in ECR plasmas, the ratio of ion flux to neutral Cl flux toward the substrate is fairly high, $\Gamma / I_{\text{CI}} > 0.1$, increasing almost linearly with decreasing $P_o$.

Chemical kinetics in Cl₂ plasmas have been modeled to gain an insight into the measured CI concentrations and to understand chemical compositions in ECR plasmas. A comparison between the measured and calculated Cl concentrations indicated that the known cross section $a$, for dissociative excitation of Cl₂ may be excessively large, by about an order of magnitude. The calculated chemical compositions showed that in ECR plasmas, molecular Cl⁺ ions are still more abundant than atomic Cl ions; moreover, Cl⁻ negative ions are less abundant than plasma electrons, which is in contrast to the situation generally appreciated for rf discharges at high pressures.

Under these ECR plasma conditions, poly-Si etch rates of 1000–2000 Å/min were obtained in combination with poly-Si/SiO₂ selectivities $> 50$. The etched profiles were nearly anisotropic, exhibiting no undercutting or signature of purely chemical etching; in practice, some lateral etching was observed after an overetch step, particularly at higher $P_o$. Such highly directional, highly selective etching in ECR is ascribed primarily to high ion-to-neutral flux ratios $\Gamma / I_{\text{CI}}$ onto the substrate and to low energies of the incoming ions. The etch rate behavior may be well expressed in terms of an adsorption-reaction-ion stimulated desorption process, assuming the incoming low-energy ions as well as neutrals to be adsorbed on surfaces. Moreover, the lateral etching in ECR may be interpreted in terms of the incoming ion trajectories affected by localized charging of pattern features.

The problems contained in this paper tend to be generic to all low-pressure, high-density plasma etching, although many of them remain unresolved.

References